AIR POLLUTION

1. Introduction

Air pollution is the presence of any substance in the atmosphere at a concentration high enough to produce an undesirable effect on humans, animals, vegetation, or materials, or to significantly alter the natural balance of any ecosystem. Air pollutants can be solids, liquids, or gases, and can be produced by anthropogenic activities or natural sources. In this article, only nonbiological material is considered and the discussion of airborne radioactive contaminants is limited to radon [10043-92-2], which is discussed in the context of indoor air pollution.

Concern about the effects of atmospheric contaminants on human health and the environment can be traced for centuries. For example, laws in Israel

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in the first and second centuries AD required that tanneries be located downwind of towns (1). In the fourteenth century, protests over the burning of sea coal resulted in the taxation of coal, and men were tortured for producing a pestilent odor. In the United States, the first air pollution regulations also dealt with coal. Cities such as Chicago, St. Louis, and Cincinnati passed smoke ordinances in the nineteenth century. In the early twentieth century, concern about the impacts of air pollution can be traced to severe episodes, which demonstrated that air pollutants can be hazardous to human health and can even cause death at high enough concentrations. For example, a week-long air stagnation in the Meuse Valley in Belgium in 1930 led to the death of 60 people and respiratory problems for a large number of others. In 1948, similar conditions in Donora, Pennsylvania, resulted in nearly 7000 illnesses and 20 deaths, and in 1952, 4000 deaths were attributed to a 4-day "killer fog" in London, England. The episodes dramatized the acute health effects of high concentrations of air pollutants, but these are rare events.

Over the past several decades concern about air pollutants has evolved; the current focus is on the effects of long term, chronic exposures to nonlethal concentrations of air pollutants, the effects of air pollution on global and regional climate, and the effects of air pollutants on global and regional atmospheric cycles (eg, stratospheric ozone depletion and acid deposition).

Health effects associated with chronic exposure to air pollution is a worldwide problem. The World Health Organization (WHO) has estimated that ~2.7 million deaths are attributable to air pollution throughout the world each year.

Table 1. **Air Quality in Mega-Cities (2)**

City	SO_2	SPM	Pb	CO	NO_2	O_3	Year in which data were collected
Athens	[a]	no data	no data	[a]	[b]	[a]	1995
Bangkok	[a]	[b]	[a]	no data	[a]	no data	1995
Beijing	[b]	[b]	no data	no data	no data	no data	1994
Bucharest	[a]	[c]	[b]	no data	[c]	no data	1995
Calcutta	[a]	[b]	no data	no data	[a]	no data	1995
Caracas	[a]	[c]	[b]	no data	[c]	no data	1995
Delhi	[a]	[b]	no data	no data	[c]	no data	1995
Johannesburg	[a]	[a]	[b]	[a]	[a]	[a]	1994
London	[a]	[a]	[a]	[a]	[c]	[a]	1995
Los Angeles	[a]	[c]	[a]	[a]	[a]	[c]	1995
Mexico City	[a]	[b]	no data	no data	[c]	[b]	1993
Santiago	[a]	[b]	no data	[a]	[c]	[a]	1995
Sofia	[a]	[b]	[a]	no data	[b]	no data	1995
Shanghai	[c]	[b]	no data	no data	no data	no data	1994
Sydney	no data	[a]	[a]	[a]	[a]	[a]	1995
Tokyo	[a]	[c]	[a]	[a]	[c]	[a]	1995
Xian	[c]	[b]	no data	no data	no data	no data	1994

[a] Low pollution—WHO guidelines are normally met.

[b] Moderate to heavy pollution—WHO guidelines exceeded by up to a factor of 2.

[c] Serious problem—WHO guidelines exceeded by more than a factor of 2.

Among the air pollutants of greatest concern are ozone, suspended particulate matter, nitrogen dioxide, sulfur dioxide, carbon monoxide, lead, and other toxins (detailed descriptions of these air pollutants are provided in subsequent sections). Of these pollutants, ozone is one of the most prevalent air pollutants in large cities and has been associated with increased respiratory illness and decreased lung function, particularly in children. Suspended particulate matter is the air pollutant most responsible for mortality worldwide. A review of the distribution and concentration of air pollutants, worldwide, is available from the WHO and is summarized in Table 1.

In addition to concerns about localized health impacts of urban air pollution, there has been a growing recognition of regional and global impacts of air pollutants on the natural balances of the earth's systems and on climate. This article will describe three examples of impacts of air pollutants on natural balances of the earth's systems: stratospheric ozone depletion, global climate change, and acid deposition.

The remainder of this article is organized into three major sections, which describe the sources and impacts of specific air pollutants, the regional and global impacts of air pollutants, and the air quality management and regulatory system in the United States.

2. Air Pollutants

Air pollution is a complex mixture of many chemical species, and any description of air pollution must account for that heterogeneity. The description of air pollutants presented here begins with a discussion of photochemical smog, defined broadly, then focuses on specific pollutants that are the targets of regulations in the United States. These include volatile organic compounds (VOCs), oxides of nitrogen (NO_x, primarily NO and NO_2), sulfur oxides (SO_x, primarily SO_2), carbon monoxide, lead, and air toxics. Finally, a description of indoor air pollutants is provided.

2.1. Photochemical Smog.

Photochemical smog is a complex mixture of constituents that are emitted directly to the atmosphere (primary pollutants) and constituents that are formed by chemical and physical transformations that occur in the atmosphere (secondary pollutants). Ozone (O_3), is generally the most abundant species formed in photochemical smog. Ozone is a secondary pollutant formed by the reactions of hydrocarbons and NO_x. Extensive studies have shown that O_3 is both a lung irritant and a phytotoxin. It is responsible for crop damage and is suspected of being a contributor to forest decline in Europe and in parts of the United States. There are, however, a multitude of other photochemical smog species that also have significant environmental consequences. The most important of these pollutants are particles, hydrogen peroxide (H_2O_2), [7722-84-1], peroxyacetyl nitrate (PAN) ($C_2H_3NO_5$), [2278-22-0], aldehydes, and nitric acid (HNO_3), [7697-37-2]. All of these pollutants are secondary, produced in the atmosphere by the reactions of precursor species (although some types of particles, such as diesel soot, are emitted directly).

Since many components of photochemical smog are secondary, government regulatory agencies have attempted to reduce the incidence of smog episodes by controlling the emissions of precursor species. In the case of ozone, these precursor species are reactive hydrocarbons and nitrogen oxides. The mechanism for the production of ozone is generally initiated by the photolysis of nitrogen dioxide. In the presence of sunlight, $h\nu$, NO_2 photolyzes, producing NO and atomic oxygen. The atomic oxygen reacts with O_2 to produce O_3

$$NO_2 + h\nu \rightarrow NO + O\,(^3P) \tag{1}$$

$$O + O_2 + M \rightarrow O_3 + M \tag{2}$$

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{3}$$

where O (^{3}P) is a ground-state oxygen atom and M is any third body molecule (most likely N_2 or O_2 in the atmosphere) that remains unchanged in the reaction. This process produces a steady-state concentration of O_3 that is a function of the concentrations of NO and NO_2, the solar intensity, and the temperature.

$$[O_3] = k\,[NO_2]/[NO]$$

where $[O_3]$, $[NO_2]$, and [NO] are the atmospheric concentrations of ozone, nitrogen dioxide, and nitric oxide and k is a constant dependent on temperature and solar intensity.

Although these reactions are extremely important in the atmosphere, the steady-state O_3 produced by the reactions of nitrogen oxides alone is much lower than the observed concentrations, even in clean air. In order for ozone to accumulate, there must be a mechanism that converts NO to NO_2 without consuming a molecule of O_3, as does reaction 3. Reactions involving hydroxyl radicals and hydrocarbons constitute such a mechanism. In clean air OH may be generated by

$$O_3 + h\nu \rightarrow O_2 + O\,(^1D) \tag{4}$$

$$O(^1D) + H_2O \rightarrow 2\,OH \tag{5}$$

where O(^{1}D) is an excited form of an O atom that is produced from a photon at a wavelength between 280 and 310 nm. This seed OH can then participate in a chain reaction with hydrocarbons. The reactions with methane are shown below.

$$OH + CH_4 \rightarrow H_2O + CH_3 \tag{6}$$

$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M \tag{7}$$

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2 \tag{8}$$

One of the outcomes of reactions 6–8 is the conversion of NO into NO_2. NO_2 can then photolyze producing O_3 (eqs. 1 and 2) and less NO is available to scavenge the ozone (eq. 3), resulting in a higher steady state ozone concentration. In addition, the CH_3O radical continues to react:

$$CH_3O + O_2 \rightarrow HCHO + HO_2 \tag{9}$$

$$HO_2 + NO \rightarrow NO_2 + OH \tag{10}$$

Reactions 9 and 10 result in an additional NO to NO_2 conversion and the regeneration of the hydroxyl radical.

Further, the formaldehyde photodissociates:

$$HCHO + h\nu \rightarrow H_2 + CO \tag{11}$$

$$\rightarrow HCO + H \tag{12}$$

$$HCO + O_2 \rightarrow HO_2 + CO \tag{13}$$

$$H + O_2 \rightarrow HO_2 \tag{14}$$

and the HO_2 from both equations 13 and 14 can form additional NO_2. Moreover, CO can be oxidized:

$$CO + OH \rightarrow CO_2 + H \tag{15}$$

and the H radical can form another NO_2 (eqs. 14 and 10). Thus, the oxidation of one CH_4 molecule is capable of producing three O_3 molecules and two OH radicals. The routes involve both the direct reactions of methane and the reactions of its oxidation products.

Finally, the chain reactions can be terminated by radical–radical recombination, or by radical reactions with more stable species. Two examples are given below.

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \tag{16}$$

$$OH + NO_2 \rightarrow HNO_3 \tag{17}$$

Examination of reactions 6–17 reveals that the chemical sequence initiated by the reaction of hydroxyl radical with a hydrocarbon can lead to the enhancement of ozone concentration, by converting NO to NO_2, and the generation of additional free radicals. The chemistry is complex and depends on the reactions of both the original hydrocarbon species and its reaction products. Because of the complexity of the reactions it is common to characterize the ozone formation potential of hydrocarbons using the parameters shown in Table 2. These parameters are the rate of reaction of a hydrocarbon with hydroxyl radical, and the incremental reactivity of the hydrocarbon.

The rate of reaction of the hydrocarbon with hydroxyl radical characterizes the rate at which the initial reaction (analogous to reaction 6) occurs, and is expressed in Table 2 as the rate constant for the bimolecular reaction with hydroxyl radical, in units of cm^3/molecule/s. In general, internally bonded olefins are the most reactive, followed in decreasing order by terminally bonded olefins,

Table 2. **Reactivities of VOCs**

Compound	CAS Registry Number	Rate constant for reaction with OH × 10^{12} (cm^3/molecule/s/)	Incremental reactivity (grams ozone formed per gram VOC added to a base mixture)
methane	[74-82-8]	0.01	0.0139
isopentane	[78-78-4]	3.7	1.67
n-butane	[106-97-8]	2.44	1.33
toluene	[108-88-3]	3.8	3.97
propane	[74-98-6]	1.12	0.56
ethane	[78-84-0]	0.254	0.31
n-pentane	[109-66-0]	4.0	1.54
ethylene	[74-85-1]	8.5	9.08
m-xylene	[108-38-3]	20	10.61
p-xylene	[106-42-3]	10	4.25
2-methylpentane	[107-83-5]	5.3	1.80
isobutane	[75-28-5]		1.35
propylene	[115-07-1]	26.3	11.58
isoprene	[78-79-5]	101	10.69

multialkyl aromatics, monoalkyl aromatics, C_5 and higher paraffins, C_2–C_4 paraffins, benzene, acetylene, and ethane (3–5).

The incremental reactivity (6, 7) characterizes the ozone formation potential of the hydrocarbon and all of its reaction products. It is expressed as grams of ozone formed per gram of hydrocarbon added to a mixture and is determined by adding an incremental amount of hydrocarbon to a base mixture of hydrocarbons typically found in urban areas, and determining the incremental amount of ozone formed. This incremental reactivity depends on the composition of the base mixture. The values shown in Table 2 are the maximum values of the incremental reactivities for each of the hydrocarbons. Values tend to be highest for species that produce reaction products that are also highly reactive.

The ozone formation reactions summarized in reactions 1–17 are driven by solar radiation. Once the sun sets, O_3 formation ceases and, in an urban area, ozone is rapidly scavenged by freshly emitted NO (eq. 3). On a typical summer night, however, a nocturnal inversion begins to form around sunset, usually below a few hundred meters and consequently, the surface-based NO emissions are trapped below the top of the inversion. Above the inversion to the top of the mixed layer (usually ~1500 m), O_3 is depleted at a much slower rate. The next morning, the inversion dissipates and the O_3-rich air aloft is mixed down into the O_3-depleted air near the surface. This process, in combination with the onset of photochemistry as the sun rises, produces the sharp increase in surface O_3 shown in Figure 1. The overnight O_3 depletion is less in the more rural areas than in a large urban area such as New York City, which is a result of the lower overnight levels of NO in rural areas. Even in the absence of NO or other O_3 scavengers (olefins, eg), O_3 decreases at night near the ground faster than aloft because of its deposition on the ground, buildings, and trees. At the remote mountaintop sites, Whiteface and Utsayantha, there is no overnight decrease in O_3 concentrations.

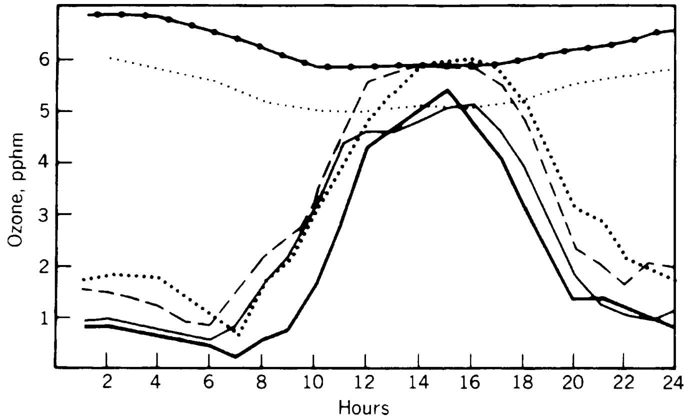


Fig. 1. Ozone formation over the course of a day. Courtesy of Air and Waste Management Association.

Although photochemical smog is a complex mixture of many primary and secondary pollutants and involves a myriad of atmospheric reactions, there are characteristic pollutant concentration versus time profiles that are generally observed within and downwind of an urban area during a photochemical smog episode. In particular, the highest O_3 concentrations are generally found 10–100 km downwind of the major emission sources, unless the air is completely stagnant. This fact, in conjunction with the long lifetime of O_3 in the absence of high concentrations of NO, means that O_3 is a regional air pollution problem. In the Los Angeles basin, high concentrations of O_3 are transported throughout the basin and multiday episodes are exacerbated by the accumulation of O_3 aloft that is then mixed to the surface daily. On the east coast, a typical O_3 episode is associated with a high pressure system anchored offshore producing a southwesterly flow across the region. As a result, emissions from Washington, D.C. travel and mix with emissions from Baltimore and over a period of a few days continue traveling northeastward through Philadelphia, New York City, and Boston. Under these conditions, the highest O_3 concentrations typically occur in central Connecticut (9).

In order to reduce O_3 in a polluted atmosphere, reductions in the VOC and NO_x precursors are required. However, the choice of whether to control VOC, or NO_x, or both depends on the local VOC/NO_x ratio. At low VOC/NO_x ratios, O_3 formation is suppressed through equations 3 and 17. Consequently, in this case reducing NO_x emissions, emitted mainly as NO, reduces the amount of O_3 (eq. 3) and OH (eq. 17) scavenged, increasing the O_3 concentrations.

The dependence of ozone formation on VOC/NO_x ratios is often presented using an ozone isopleth diagram. An example of this type of diagram is illustrated in Figure 2. The diagram plots contours of the maximum ozone concentration achieved as a function of the initial VOC and NO_x concentrations in the mixture. The key features of the ozone isopleth diagram are summarized in Figure 3. The region in the upper left is the NO_x--inhibition region where a decrease

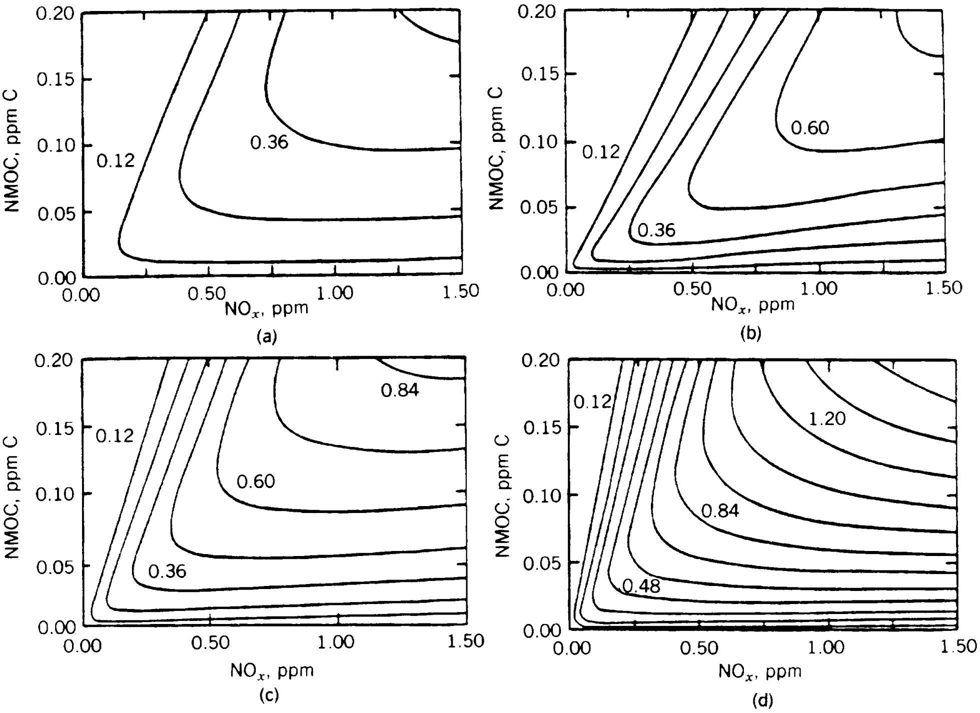


Fig. 2. Examples of ozone isopleths generated using four different chemical mechanisms (**a**) EPA; (**b**) FSM; (**c**) CBII; (**d**) ELSTAR; NMOC = nonmethane organic compounds (10). Courtesy of Pergamon Press.

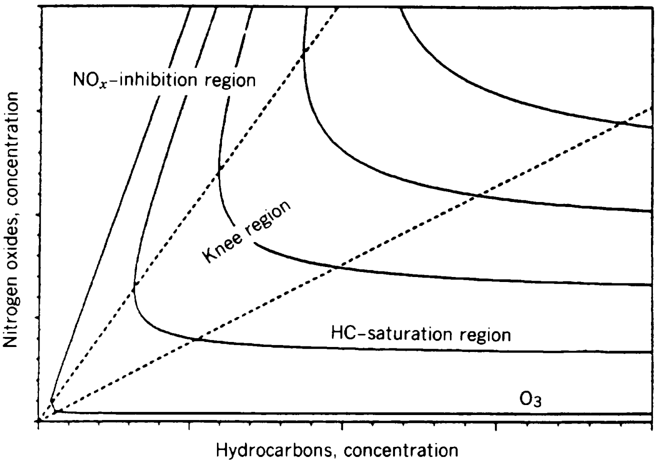


Fig. 3. Typical O_3 isopleth diagram showing the three chemical regimes; HC = hydrocarbons (11). Courtesy of Pergamon Press.

in NO_x alone results in an increase in O_3, but a decrease in VOC decreases O_3. The region at the bottom right is the hydrocarbon (HC) or VOC saturation region where reducing VOCs has no effect on the O_3 level. Here, a reduction in NO_x results in lower O_3. In the middle is the knee region, where reductions in either NO_x or VOC reduce O_3. The upper boundary of this region varies from day to day and from place to place as its location is a function of the reactivity of the VOC mix and the sunlight intensity.

As a guideline, VOC controls are generally the most efficient way to reduce O_3 in areas having a median VOC/NO_x ratio of 10:1 or less (measured between 6 and 9 a.m.); whereas areas with a higher ratio may need to consider NO_x reductions as well (12). The 1990 Clean Air Act Amendments require that O_3 nonattainment areas reduce both VOC and NO_x from major stationary sources unless the air quality benefits are greater in the absence of NO_x reductions. Large cities in the northeast tend to have ratios <10:1; cities in the south (Texas and eastward) tend to have ratios >10:1. Determining a workable control strategy is further complicated by the transport issue. For example, on high O_3 days in the northeast, the upwind air entering Philadelphia and New York City frequently contains high concentrations of O_3 as a result of emissions from areas to the west and south (13). Consequently, control strategies must be developed on a coordinated, multistate regional basis.

While the focus of this discussion has been ozone, ozone can be considered as a surrogate for the wide variety of chemical species found in photochemical smog. For example, H_2O_2, formed via reaction 16, is important because when dissolved in cloud droplets it is an important oxidant, responsible for oxidizing SO_2 to sulfuric acid (H_2SO_4), [7664-93-9], the primary cause of acid precipitation. The oxidation of many VOCs produces acetyl radicals, CH_3CO, which can react with O_2 to produce peroxyacetyl radicals, $CH_3(CO)O_2$, which react with NO_2

$$CH_3(CO)O_2 + NO_2 \leftrightarrow CH_3(CO)O_2NO_2(PAN) \tag{18}$$

At high enough concentrations, PAN is a potent eye irritant and phytotoxin. On a smoggy day in the Los Angeles area, PAN concentrations are typically 5–10 ppb; in the rest of the United States PAN concentrations are generally a fraction of a ppb. An important formation route for formaldehyde (HCHO), [50-00-0], is the oxidation of hydrocarbons (analogous to reaction 9). However, ozonolysis of olefinic compounds and some other reactions of VOCs can also produce HCHO and other aldehydes. Aldehydes are important because they are temporary reservoirs of free radicals (see eqs. 11 and 12). HCHO is a known carcinogen. Nitric acid is formed by OH attack on NO_2 and by a series of reactions initiated by $O_3 + NO_2$. Nitric acid is important because it is the second most abundant acid in precipitation. In addition, in southern California it is the major cause of acid fog.

Particles are the major cause of the haze that is often associated with smog. The three most important components of particles produced in smog are organics, sulfates, and nitrates. Organic particles are formed when large VOC molecules, especially aromatics and cyclic alkenes, react and form condensable products. Sulfate particles are formed by a series of reactions initiated by the attack of OH on SO_2 in the gas phase or by liquid-phase reactions. Nitrate particles are formed by

$$HNO_{3(g)} + NH_3 \leftrightarrow NH_4NO_{3(s)} \tag{19}$$

or by the reactions of HNO_3 with NaCl or alkaline soil dust.

2.2. Volatile Organic Compounds. VOCs include any organic carbon compound that exists in the gaseous state in the ambient air. In some of the older literature the term VOC is used interchangeably with nonmethane hydrocarbons (NMHC). Reactive organic gases is also a term that is sometimes used to refer to a subset of VOCs that are reactive with hydroxl radical. VOC sources may be any process or activity utilizing organic solvents, coatings, or fuel. Emissions of VOCs are important: some are toxic by themselves, and most are precursors of O_3 and other species associated with photochemical smog. As a result of control measures designed to reduce O_3, VOC emissions are declining in the United States. Figure 4 shows estimates of nationwide emissions of VOCs (14). Emissions peaked ~1970 and have declined by ~40% from that peak. Major sources continue to be industrial processes, solvent use (including solvents used in architectural coatings such as paints and varnishes), non-road sources (such as marine and garden equipment engines) and vehicular sources. This national compilation of VOC emission sources may underestimate the contribution from on-road vehicles, but exhibits the general trends observed in the emissions.

2.3. Nitrogen Oxides (NO_x). Most of the NO_x is emitted as NO, which is then oxidized to NO_2 in the atmosphere (see eqs. 3 and 8). All combustion processes are sources of NO_x. At the high temperatures generated during combustion, some N_2 is converted to NO in the presence of O_2 and, in general, the higher the combustion temperature, the more NO_x produced. Emissions of NO_x have remained relatively constant since the mid-1970s, and the major sources

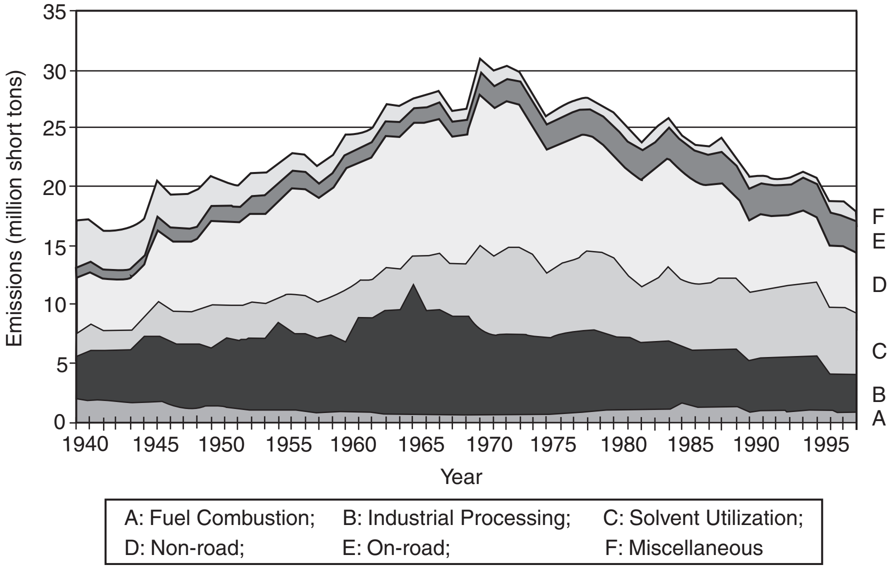


Fig. 4. Trends in emissions of VOCs 1940–1998 (14).

continue to be combustion in industrial facilities, electric power generation, nonroad engines (especially construction equipment) and on-road vehicles.

NO_x emissions remain an important issue throughout the United States. As emissions of VOCs have decreased, reducing emissions of NO_x has become a more important component of ozone control strategies in the United States. In addition to being an essential ingredient of photochemical smog and a precursor to HNO_3, itself an ingredient of acid precipitation and fog, NO_2 is the only important gaseous species in the atmosphere that absorbs visible light. In high enough concentrations it can contribute to a brownish discoloration of the atmosphere (see Fig. 5.)

2.4. Sulfur Oxides (SO_x). The combustion of sulfur-containing fossil fuels, especially coal, is the major source of SO_x. Between 97 and 99% of the SO_x emitted from combustion sources is in the form of SO_2. The remainder is mostly sulfur trioxide (SO_3), [7446-11-9], which in the presence of atmospheric water [7732-18-5] vapor is immediately transformed into H_2SO_4, a liquid particulate. Both SO_2 and H_2SO_4 at sufficient concentrations produce deleterious effects on the respiratory system. In addition, SO_2 is a phytotoxin. Control strategies designed to reduce the ambient levels of SO_2 have been highly successful. In the 1960s, most industrialized urban areas in the eastern United States had an SO_2 air quality problem. Now there are no areas that exceed the SO_2 national ambient air quality standards. Over the period 1990–1999, nationwide emissions of SO_2 declined 21% and ambient concentrations decreased 36% (14). However, additional SO_2 reductions are required because of the role that SO_2 plays in acid deposition. In addition, there is some concern over the health effects of H_2SO_4 particles, which are emitted directly from some sources as well as being formed in the atmosphere.

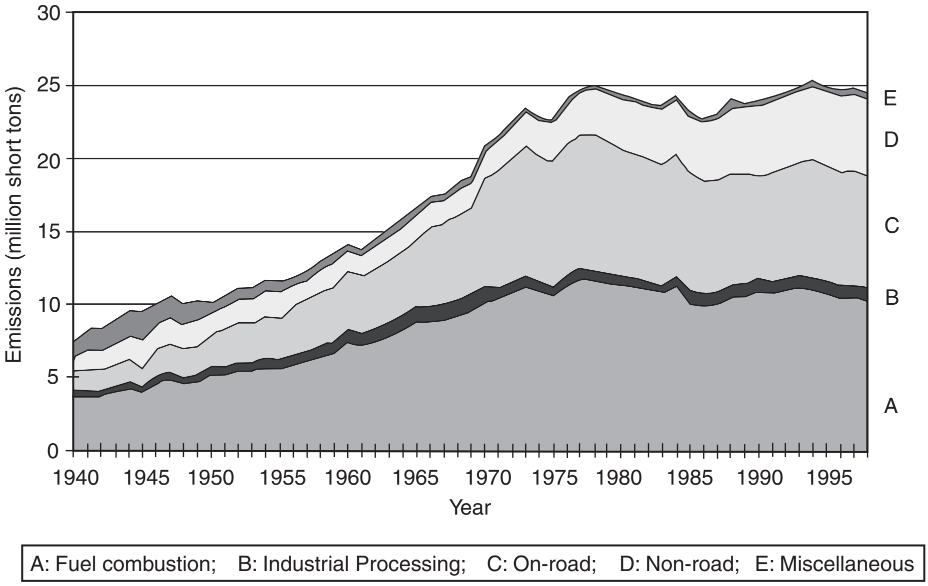


Fig. 5. Trends in emissions of NO_x 1940–1998 (14).

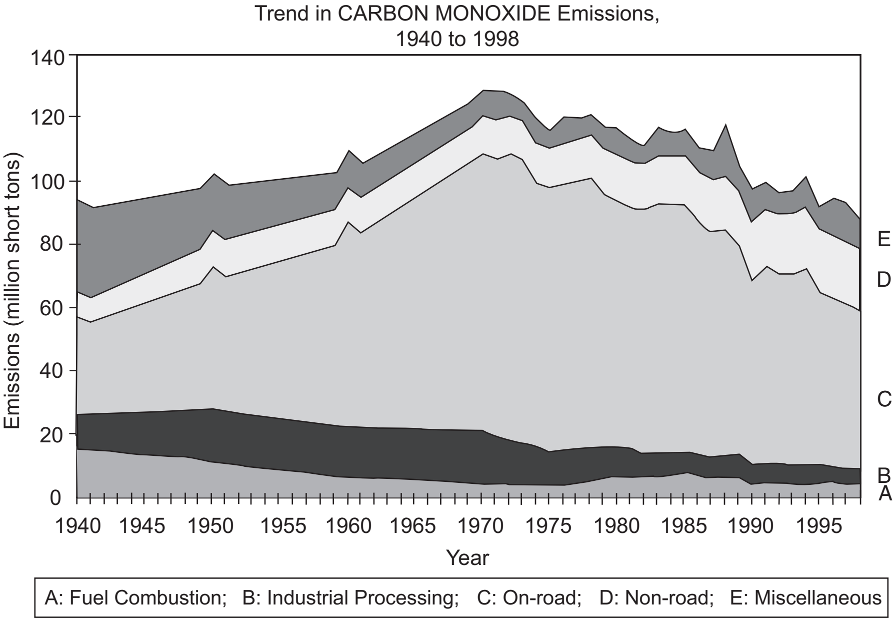


Fig. 6. Trends in emissions of CO, 1940–1998 (14).

2.5. Carbon Monoxide. Carbon monoxide is emitted during any combustion process. Transportation sources account for about two-thirds of the CO emissions nationally, but, in certain areas, significant quantities of CO come from woodburning fireplaces and stoves. CO is absorbed through the lungs into the blood stream and reacts with hemoglobin [9034-51-9] to form carboxyhemoglobin, which reduces the oxygen carrying capacity of the blood.

As shown in Figure 6, emissions of CO in the United States peaked in the late 1960s, but have decreased consistently since that time as transportation sector emissions significantly decreased. Between 1968 and 1983, CO emissions from new passenger cars were reduced by 96%. This has been partially offset by an increase in the number of vehicle-miles traveled annually. Even so, there has been a steady decline in the CO concentrations across the United States. From 1980–1999, CO concentrations decreased by an average of 57% and during the 1990s the decrease was 36% (14).

2.6. Particulate Matter. Solid- and liquid-phase material in the atmosphere is variously referred to as particulate matter, particulates, particles, and aerosols. These terms are often used interchangeably. The original air quality standards in the United States were for total suspended particulates, (TSP), the weight of any particulate matter collected on the filter of a high volume air sampler. On the average, these samplers collect particles that are less than about 30–40 μm in diameter, but collection efficiencies vary according to both wind direction and speed. In 1987, the term PM_{10}, particulate matter having an aerodynamic diameter of 10 μm or less, was introduced. The 10-μm diameter was chosen because 50% of the 10-μm particles deposit in the respiratory tract below the

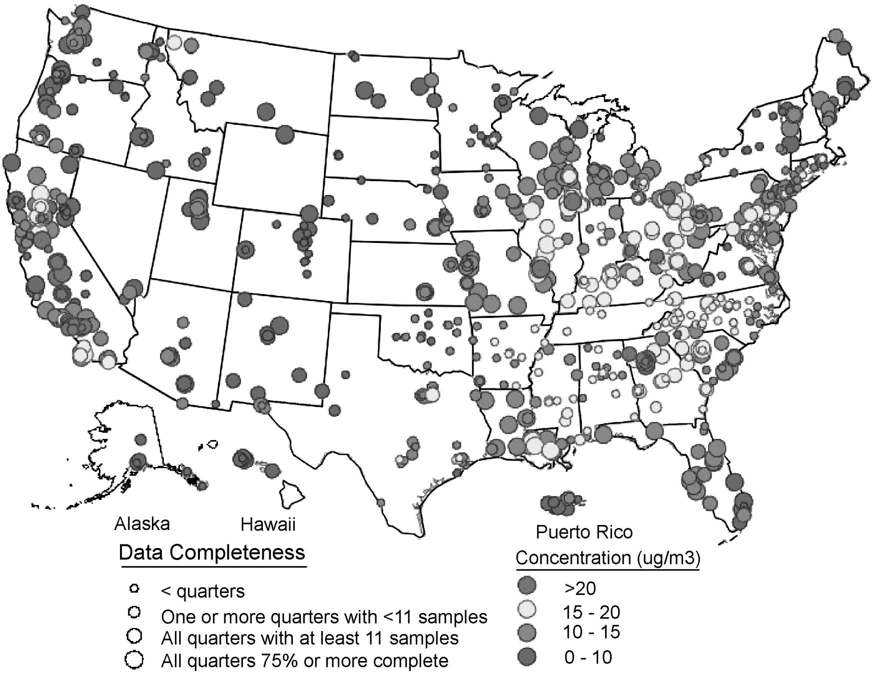
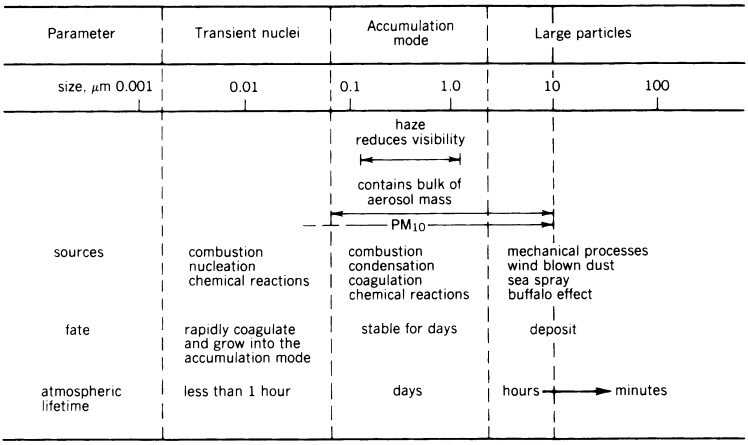


Fig. 7. Spatial distribution of fine particulate matter (14).

larynx during oral breathing. The fraction deposited decreases as particle diameter increases above 10 μm. Beginning in 1997, the term PM$_{2.5}$ (sometimes called fine particulate matter), particulate matter having an aerodynamic diameter of 2.5 μm or less, was introduced. Air quality standards for fine particulate matter were introduced in 1997 in recognition of growing evidence of the health impacts of particles that can penetrate very deeply into the respiratory system. Data on PM$_{2.5}$ concentrations are not yet widely available, but some preliminary measurements are provided in Figure 7. Ambient concentrations of PM$_{10}$ declined by 18% between 1990 and 1999. Data on ambient concentrations of PM$_{10}$ indicate a decline of 18% between 1990 and 1999 (14).

Atmospheric particulate matter can be classified into three size modes: nuclei, accumulation, and large or coarse-particle modes. Characteristics are given in Figure 8. The bulk of the aerosol mass usually occurs in the 0.1–10-μm size range, which encompasses most of the accumulation mode and part of the large-particle mode. The nuclei mode is transient as nuclei, formed by combustion, nucleation, and chemical reactions. The nulceation mode particles coagulate and grow into the accumulation mode. Particles in the accumulation mode are relatively stable because they exceed the size range where coagulation is important, and they are too small to deposit out of the atmosphere quickly. Consequently, particles "accumulate" in this mode. Particles larger than ~2.5 μm begin to have appreciable rates of sedimentation from the atmosphere, so their lifetimes in the atmosphere decrease significantly as particle size increases. The sources of large particles are mostly mechanical processes, such as dust entrainment by wind.



Parameter	Transient nuclei	Accumulation mode	Large particles
size, µm 0.001	0.01	0.1 1.0	10 100
		haze reduces visibility contains bulk of aerosol mass PM10	
sources	combustion nucleation chemical reactions	combustion condensation coagulation chemical reactions	mechanical processes wind blown dust sea spray buffalo effect
fate	rapidly coagulate and grow into the accumulation mode	stable for days	deposit
atmospheric lifetime	less than 1 hour	days	hours → minutes

Fig. 8. Some important aerosol characteristics. Data modified from Ref. 15, which was adopted in part from Ref. 16.

Figure 9 shows the mass size distribution of typical ambient aerosols. Note the mass peaks in the accumulation mode and between 0.5 and 1.0 µm. The minimum in the curves at ~1–2.5 µm results from a lack of sources for these particles. Coagulation is not significant for the accumulation-mode particles, and particles produced by mechanical process are >2.5 µm. Consequently, particles less than ~ 2.5 µm have different sources from particles >2.5 µm and it is convenient to classify PM_{10} into a coarse-particulate-mass mode (CPM, diameter range of 2.5–10 µm) and a fine-particulate-mass mode (FPM, diameter <2.5 µm). By knowing the relative amounts of CPM and FPM as well as the chemical composition of the major species, information on the PM_{10} sources can be deduced. In urban areas the CPM and FPM are usually comparable in mass; in rural areas the FPM is generally lower than in urban areas, but higher than the CPM mass. A significant fraction of the rural FPM is generally transported from upwind sources, whereas most of the CPM is generated locally.

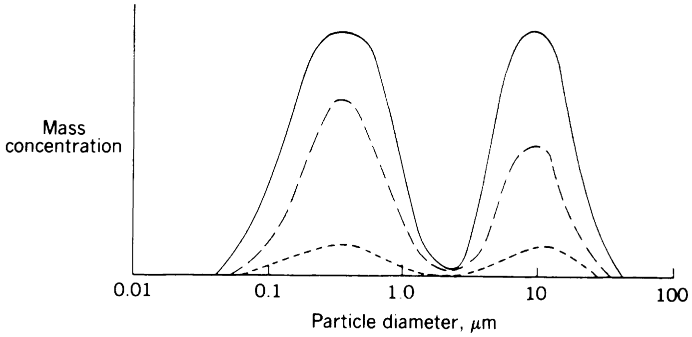


Fig. 9. Size distributions of atmospheric particles in (– –) urban, (— —) rural, and (- -) remote background areas.

Sulfate (SO_4^{2-}), carbon (as organic carbon, OC, and elemental carbon, EC), and nitrate (NO_3^-) compounds generally account for 70–80% of the FPM. In the eastern United States, SO_4^{2-} compounds are the dominant species, although very little SO_4^{2-} is emitted directly into the atmosphere. Thus most of the sulfate is a secondary aerosol formed from the oxidation of SO_2, and in the eastern United States coal-burning emissions are the source of most of the SO_2.

In the atmosphere, the principal SO_2 oxidation routes include homogeneous oxidation by OH, and the heterogeneous oxidation in water droplets by H_2O_2, O_3, or, in the presence of a catalyst, O_2. Atmospheric particles that have been identified as catalysts include many metal oxides and soot. The water droplets include cloud and dew droplets as well as aerosols that contain sufficient water: under high relative-humidity conditions, hygroscopic salts deliquesce, and form liquid aerosols. Sulfuric acid is the initial SO_2 oxidation product. This rapidly reacts with any available ammonia [7664-41-7], NH_3 to form ammonium bisulfate [7803-63-6], NH_4HSO_4. If sufficient NH_3 is present, the final product is ammonium sulfate [7783-20-2], $(NH_4)_2SO_4$. In some urban areas in the western United States, NO_3^- is more abundant than SO_4^{2-}. The NO_3^- in the FPM exists primarily as ammonium nitrate, NH_4NO_3, [6484-52-2] (see eq. 19). However, acidic SO_4^{2-} (H_2SO_4 or NH_4HSO_4) readily reacts with NH_4NO_3 and abstracts the NH_3, leaving behind gaseous HNO_3. Consequently, unless there is sufficient NH_3 to completely convert all of the SO_4^{2-} to $(NH_4)_2SO_4$, NH_4NO_3 does not accumulate in the atmosphere.

Organic compounds are a major constituent of the FPM at all sites. The major sources of OC are combustion and atmospheric reactions involving gaseous VOCs. As is the case with VOCs, there are hundreds of different OC compounds in the atmosphere. A minor but ubiquitous aerosol constituent is elemental carbon (EC), which is the nonorganic, black constituent of soot. Combustion and pyrolysis are the only processes that produce EC, and diesel engines and wood burning are the most significant sources.

Crustal dust and water make up most of the remaining FPM mass. Crustal dust is composed of aerosolized soil and rock from the earth's crust. Although this is natural material, human activities (traffic, which entrains street dust, construction activities, agricultural and land-use practices, etc) affect the rate at which crustal material is aerosolized. Since it is aerosolized by frictional processes, the diameter of most of the crustal dust is > 2.5 μm and typically accounts for most of the CPM and particle mass < 10 μm. In global average crustal material, the major elements contained in decreasing order are O, Si, Al, Fe, Ca, Na, K, and Mg. Consequently, the crustal mass can be estimated from Si measurements alone. However, the relative amounts of the elements do vary spatially.

2.7. Lead. Lead is of concern because of its tendency to be retained by living organisms. When excessive amounts accumulate in humans, lead can inhibit the formation of hemoglobin and produce life-threatening lead poisoning. In smaller doses, lead is also suspected of causing learning disabilities in children. From 1980 to 1999, nationwide Pb emissions decreased 95%. This reduction is a direct result of the removal of lead compounds such as tetraethyllead $(C_2H_5)_4Pb$ [78-00-2] from fuels, primarily gasoline.

2.8. Air Toxics. There are thousands of commercial chemicals used in the United States. Hundreds are emitted into the atmosphere and have some potential to adversely affect human health at certain concentrations; some are known or suspected carcinogens. Identifying all of these substances and promulgating emissions standards is beyond the present capabilities of existing air quality management programs. Consequently, toxic air pollutants (TAPs) need to be prioritized based on risk analysis, so that those posing the greatest threats to health can be regulated.

The 1970 Clean Air Act required that EPA provide an ample margin of safety to protect against hazardous air pollutants (HAPs) by establishing national emissions standards for certain sources. From 1970 to 1990, over 50 chemicals were considered for designation as HAPs, but EPAs review process was completed for only 28 chemicals. However, in the 1990 Clean Air Act Amendments, 189 substances are listed that EPA must regulate by enforcing maximum achievable control technology (MACT). The Amendments mandate that EPA issue MACT standards for all sources of the 189 substances. In addition, EPA must determine the risk remaining after MACT is in place and develop health-based standards that would limit the cancer risk. EPA may add or delete substances from this list.

2.9. Indoor Air Pollution. Indoor air pollution, the presence of air pollutants in indoor air, is of growing concern in offices and residential buildings. Partly in response to the “energy crisis” of the early 1970s, buildings are now constructed more air-tight. Unfortunately, air-tight structures create a setting conducive to the accumulation of indoor air pollutants. Numerous sources and types of pollutants found indoors can be classified into eight categories: tobacco smoke, radon, emissions from building materials, combustion products from inside the building, pollutants which infiltrate from outside the building, emissions from products used within the home, pollutants formed by reactions indoors, and biological pollutants. Concentrations of the pollutants depend on strength of the indoor sources, the ventilation rate of the building, and the outdoor pollutant concentration.

Tobacco smoke contains a variety of air pollutants. In a survey of 80 homes in an area where the outdoor TSP varied between 10 and 30 $\mu g/m^3$, the indoor TSP was the same, or less, in homes having no smokers. In homes having one smoker, the TSP levels were between 30 and 60 $\mu g/m^3$, while in homes having two or more smokers, the levels were between 60 and 120 $\mu g/m^3$ (17). In other studies, indoor TSP levels exceeding 1000 $\mu g/m^3$ have been found in homes with numerous smokers. In addition to TSP, burning tobacco emits CO, NO_x, formaldehyde [50-00-0], benzopyrenes, nicotine [54-11-5], phenols, and some metals such as cadmium [7440-43-9] and arsenic [7440-38-2] (18).

Radon-222 ^{222}Rn, [14859-67-7], is a naturally occurring, inert, radioactive gas formed from the decay of radium-226 ^{226}Ra, [13982-63-3]. Because Ra is a ubiquitous, water-soluble component of the earth’s crust, its daughter product, Rn, is found everywhere. A major health concern is radon’s radioactive decay products. Radon has a half-life of 4 days, decaying to polonium-218 ^{218}Po, [15422-74-9], with the emission of an α particle. It is ^{218}Po, an α-emitter having a half-life of 3 min, and polonium-214 ^{214}Po, [15735-67-8], an α-emitter having a half-life of 1.6×10^{-4} s, that are of most concern. Polonium-218 decays to lead-214 ^{214}Pb, [15067-28-4], a β-emitter having $t_{1/2} = 27$ min, which decays to bismuth-214 ^{214}Bi, [14733-03-0], a β-emitter having $t_{1/2} = 20$ min, which decays to ^{214}Po. Radon is an inert gas that, when inhaled, is not retained in the lungs. But the Rn daughters, when inhaled, either by themselves or attached to an airborne particle, are retained and the subsequent α-emissions irradiate the surrounding lung tissue.

Radon can enter buildings through emissions from soil, water, or construction materials. The soil route is by far the most common, and construction material the least common, although there have been isolated incidents where construction materials contained high levels of Ra. The emission rate of Rn depends on the concentration of Ra in the soil, the porosity of the soil, and the permeability of the building's foundation. For example, Rn is transported faster through cracks and sumps in the basement floor than through concrete. In the ambient air Rn concentrations are typically 9.25–37 mBq/L, whereas the mean concentration in U.S. residences is about 44 mBq/L (19). However, it is estimated that there are 1 million residences that have concentrations exceeding 0.3 Bq/L or 300 mBq/L, which is the level for remedial action recommended by the National Council on Radiation Protection and Measurements (19). The highest values ever measured in U.S. homes exceeded 37 Bq/L (20). Remedial action consists of (*1*) reducing the transport of Rn into the building by sealing cracks with impervious fillers and installing plastic or other barriers that have proven effective; (*2*) removing the daughters from the air by filtration; and (*3*) increasing the infiltration of outside air using an air-exchanger system.

Of the pollutants emitted from construction materials within the home, asbestos [1332-21-4] has received the most attention. Asbestos is a generic term for a number of naturally occurring fibrous hydrated silicates. By EPA's definition, a fiber is a particle that possesses a 3:1 or greater aspect ratio (length: diameter). The family of asbestos minerals is divided into two types: serpentine [12168-92-2] and amphibole. One type of serpentine, chrysotile, $Mg_6Si_4O_{10}(OH)_8$, [12001-29-5], accounts for 90% of the world's asbestos production. The balance of the world's production is accounted for by two of the amphiboles: amosite $Fe_5Mg_2Si_8O_{22}(OH)_2$, [12172-73-5], and crocidolite, $Na_2(Fe^{3+})_2(Fe^{2+})_3Si_8O_{22}(OH)_2$, [12001-28-4]. Three other amphiboles, anthophyllite $(Mg,Fe)_7Si_8O_{22}(OH)_2$, [77536-67-5], tremolite $Ca_2Mg_5Si_8O_{22}(OH)_2$, [77536-68-6] and actinolite $Ca_2(Mg,Fe)_5Si_8O_{22}(OH)_2$, [77536-66-4], have been only rarely mined. The asbestos minerals differ in morphology, durability, range of fiber diameters, surface properties, and other attributes that determine uses and biological effects. Known by ancients as the magic mineral because of its ability to be woven into cloth, its physical strength, and its resistance to fire, enormous heat, and chemical attack, asbestos was incorporated into many common building products (21).

All forms of asbestos were implicated in early studies linking exposure to airborne fibers and asbestosis (pulmonary interstitial fibrosis), lung cancer, and mesothelioma (a rare form of cancer of the lung or abdomen). However, most of the asbestos-related diseases are now thought to result from exposure to airborne amphiboles rather than chrysotile, the most common asbestos type, and to fibers greater than or equal to 5 μm in length (22). In the 1970s, the spray-on application of asbestos was banned and substitutes were found for many products. Nevertheless, asbestos was used liberally in buildings for several decades, and many of them are still standing. Asbestos in building materials does not spontaneously shed fibers, but when the materials become damaged by normal decay, renovation, or demolition, the fibers can become airborne and contribute to the indoor air pollution problem.

Formaldehyde (HCHO), [50-00-0], another important pollutant emanating from building material, is important because of irritant effects and suspected carcinogenicity. Traces of formaldehyde can be found in the air in virtually every modern home. Mobile homes and houses insulated using urea–formaldehyde [9011-05-6] foam, an efficient insulation material that can be injected into the sidewalls of conventional homes, have the highest concentrations. In 1982, use of the foam was banned in the United States. Higher formaldehyde emissions can occur in mobile homes using particle board held together using an urea–formaldehyde resin, which can also be a problem in a conventional house, but it is usually exacerbated in a mobile home because of the low rate of air exchange. Plywood is also a source of formaldehyde as the layers of wood are held together using a similar urea–formaldehyde resin adhesive. In general, however, particle board contains more adhesive per unit mass, so the emissions are greater. Other sources of indoor formaldehyde are paper products, carpet backing, and some fabrics.

Whenever unvented combustion occurs indoors or when venting systems attached to combustion units malfunction, a variety of combustion products will be released to the indoor environment. Indoor combustion units include: nonelectric stoves and ovens, furnaces, hot water heaters, space heaters, and wood-burning fireplaces or stoves. Products of combustion include CO, NO, NO_2, fine particles, aldehydes, polynuclear aromatics, and other organic compounds. Especially dangerous sources are unvented gas and kerosene [8008-20-6] space heaters that discharge pollutants directly into the living space. The best way to prevent the accumulation of combustion products indoors is to make sure all units are properly vented and properly maintained.

Pollutants from outdoors can also be drawn inside under certain circumstances such as incorrectly locating an air intake vent downwind of a combustion exhaust stack. High outdoor pollutant concentrations can also infiltrate buildings. Unreactive pollutants like CO diffuse through any openings in a building and pass unaltered through any air-intake system. Given sufficient time, the indoor/outdoor ratio for CO approaches 1.0 if outside air is the only CO source. For reactive species such as ozone, which is destroyed on contact with most surfaces, the indoor/outdoor ratio is usually < 0.5, but this ratio varies considerably depending on the ventilation rate and the internal surface area within the building (23).

Air contaminants are emitted to the indoor air from a wide variety of activities and consumer products. Most indoor activities produce some types of pollutants. When using volatile products, care should be exercised to minimize exposure through proper use of the product and by providing adequate ventilation.

Indoor air pollutants can react to form other air pollutants, perhaps most significantly, particles. Olefins found in common cleaning products, such as terpenes, can react with ozone that infiltrates from outdoors to produce particle concentrations that can exceed outdoor air quality standards.

Biological indoor air pollutants include airborne bacteria, viruses, fungi, spores, molds, algae, actinomycetes, and insect and plant parts. Microorganisms, many of which multiply in the presence of high humidity, can produce infections, disease, or allergic reactions; the nonviable biological pollutants can produce allergic reactions. The most notable episode was the 1976 outbreak of Legionella (Legionnaires') disease in Philadelphia where the American Legion convention attendees inhaled Legionella virus from a contaminated central air conditioning system. A similar incident in an industrial environment occurred in 1981: >300 workers came down with "Pontiac fever" as a result of inhalation exposure to a similar virus aerosolized from contaminated machining fluids (24). Preventive maintenance of air management systems and increased ventilation rates reduce the concentrations of all species, and should consequently reduce the incidence of adverse affects.

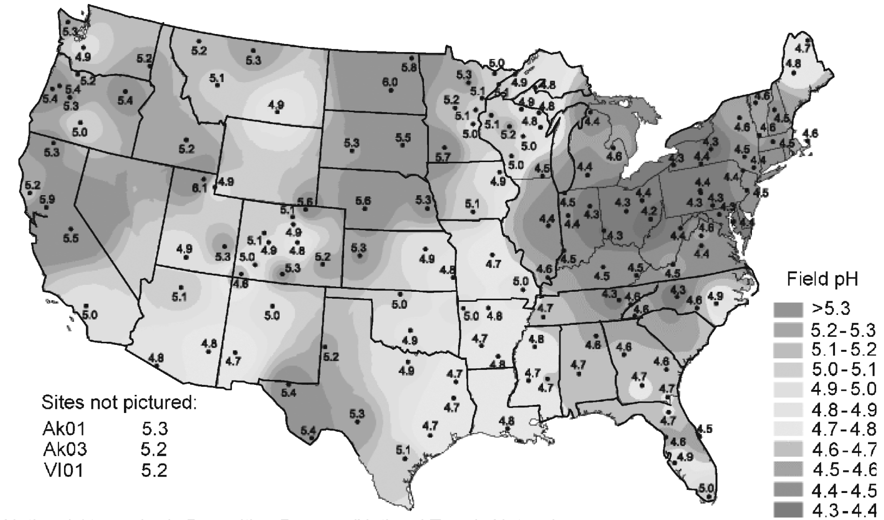
3. Regional and Global Impacts of Air Pollution

Photochemical smog is most severe in urban areas and has some impact at regional scales. There has been a growing recognition, however, that some air pollutants have impacts at regional to global scales. Three examples of impacts of air pollutants on natural balances of the earth's systems at regional and global scales are acid deposition, stratospheric ozone depletion, and global climate change.

3.1. Acid Deposition.

Acid deposition, the deposition of acids from the atmosphere to the surface of the earth, can be dry or wet. Dry deposition involves acid gases or their precursors or acid particles coming in contact with the earth's surface and then being retained. The principal species associated with dry acid deposition are $SO_2(g)$, and acid sulfate particles (H_2SO_4 and NH_4HSO_4), and $HNO_3(g)$. Measurements of dry deposition are quite sparse. On the other hand, there are abundant data on wet acid deposition. Wet acid deposition, acid precipitation, is the process by which acids are deposited by rain or snow. The principal dissolved acids are H_2SO_4 and HNO_3. Other acids, such as HCl and organic acids, usually account for only a minor part of the acidity although organic acids can be significant contributors in remote areas.

The pH of rainwater in equilibrium with atmospheric CO_2 is 5.6, a value frequently cited as the natural background pH. However, in the presence of other naturally occurring species such as SO_2, SO_4^{2-}, NH_3, organic acids, sea salt, and alkaline crustal dust, the natural values of unpolluted rainwater vary between 4.9 and 6.5 depending on time and location. Across the United States, the mean annual average precipitation pH varies from 4.2 in western Pennsylvania to 6.0 in the upper midwest (see Fig. 10). In general, precipitation of the lowest pH occurs in the summer. Precipitation pH is generally lowest in the eastern United States within and downwind of the largest SO_2 and NO_x emissions areas. In the East, SO_4^{2-} concentrations in precipitation are higher during the summer than in winter, but the NO_3^- values are about the same year round. Consequently, the lower pH in summer precipitation results mostly from the higher SO_4^{2-} concentrations. On the average in the eastern United States, $\sim 60\%$ of the wet-deposited acidity can be attributed to SO_4^{2-} and 40% to NO_3^- (25).



National Atmospheric Deposition Program/National Trends Network
http://nadp.sws.uiuc.edu

Fig. 10. Hydrogen ion concentration as pH from measurements made at the field laboratories, 1999. Spatial distribution of acid deposition (25).

3.2. Global Warming (The Greenhouse Effect).

The atmosphere allows solar radiation from the sun to pass through without significant absorption of energy. Some of the solar radiation reaching the surface of the earth is absorbed, heating the land and water. Infrared radiation is emitted from the earth's surface, but certain gases in the atmosphere absorb this infrared (ir) radiation, and redirect a portion back to the surface, thus warming the planet and making life, as we know it, possible. This process is often referred to as the *greenhouse effect*. The surface temperature of the earth will rise until a radiative equilibrium is achieved between the rate of solar radiation absorption and the rate of ir radiation emission. Human activities, such as fossil fuel combustion, deforestation, agriculture and large-scale chemical production, have measurably altered the composition of gases in the atmosphere. Recent intergovernmental panels and scientific assessments (see, eg, ref. 26) have concluded that these alterations have caused a warming of the earth-atmosphere system by enhancement of the greenhouse effect.

Table 3 is a list of the most important greenhouse gases along with their anthropogenic sources, emission rates, concentrations, residence times in the atmosphere, relative radiative forcing efficiencies, and estimated contribution to global warming. The primary greenhouse gases are water vapor, carbon dioxide, methane, nitrous oxide, chlorofluorocarbons, and tropospheric ozone. Water vapor is the most abundant greenhouse gas, but is omitted because it is not primarily due to anthropogenic sources. Carbon dioxide contributes significantly to global warming due to its high emission rate and concentration. The major factors contributing to global warming potential of a chemical are ir absorptive capacity and residence time in the atmosphere. Gases with very high absorptive capacities and long residence times can cause significant global warming even

Table 3. **Greenhouse Gases and Global Warming Contribution**[a]

Gas	Source (natural and anthropogenic)	Estimated anthro- pogenic emission rate	Preindustrial global concentration	Approximate current concentration	Estimated residence time in the atmosphere	Radiative forcing efficiency (absorptivity capacity) ($CO_2 = 1$)	Estimated contribution to global warming
carbon dioxide (CO_2)	fossil fuel combustion; deforestation	6000 *M* t/yr	280 ppm	355 ppm	50–200 yr	1	50%
methane (CH_4)	anaerobic decay (wetlands, landfills, rice patties) ruminants, termites, natural gas, coal mining, biomass burning	300–400 *M* t/yr	0.8 ppm	1.7 ppm	10 yr	58	12–19%
nitrous oxide (N_2O)	estuaries and tropical forests; agricultural practices, deforestation, land clearing, low temperature fuel combustion	4–6 *M* t/yr	0.385 ppm	0.31 ppm	140–190 yr	206	4–6%
chlorofluorocarbons (CFC-11 and CFC-12)	refrigerants, air conditioners, foam blowing agents, aerosol cans, solvents	1 *M* t/yr	0	0.0004–0.001 ppm	65–110 yr	4860	17–21%
tropospheric ozone (O_3)	photochemical reactions between VOCs and NO_x from transportation and industrial sources	not emitted directly	NA[b]	0.022 ppm	hours–days	2000	8%

[a] from ref. 27, M = million.

[b] Not applicable = NA.

though their concentrations are extremely low. A good example of this phenomenon is the chlorofluorocarbons, which are, on a pound for pound basis, >1000 times more effective as greenhouse gases than carbon dioxide.

For the past four decades, measurements of the accumulation of carbon dioxide in the atmosphere have been taken at the Mauna Loa Observatory in Hawaii, a location far removed from most human activity that might generate carbon dioxide. Based on the current level of CO_2 of 360 parts per million (ppm), levels of CO_2 are increasing at the rate of 0.5%/year (from ~320 ppm in 1960). Atmospheric concentrations of other greenhouse gases have also risen. Methane has increased from ~700 ppb in preindustrial times to 1721 ppb in 1994, while N_2O rose from 275 to 311 ppb over the same period.

While it is clear that atmospheric concentrations of carbon dioxide, and other global warming gases are increasing, there is significant uncertainty regarding the magnitude of the effect on climate that these concentration changes might induce. The relationship between atmospheric concentrations of global warming gases and climate can be separated into climate forcing (the change in net radiation due to changes in atmospheric concentrations of global warming gases) and climate response (the change in climate due to changes in heating). There is significantly less uncertainty in the understanding of climate forcing than of climate response; the Intergovernmental Panel on Climate Change (IPPC) regularly issues scientific assessments of both climate forcing and climate response.

3.3. Stratospheric Ozone Depletion.

In the stratosphere, O_3 is formed naturally when O_2 is dissociated by (uv) solar radiation in the region 180–240 nm:

$$O_2 + \text{uv} \rightarrow O + O \tag{20}$$

and the atomic oxygen then reacts with molecular oxygen according to equation 2. Ultraviolet radiation in the 200–300 nm region can also dissociate O_3:

$$O_3 + \text{uv} \rightarrow O_2 + O \tag{21}$$

Equation 21 represents the reaction responsible for the removal of uv-B radiation (280–330 nm) that would otherwise reach the earth's surface. There is concern that any process that depletes stratospheric ozone will consequently increase uv-B (in the 293–320-nm region) reaching the surface. Increased uv-B is expected to lead to increased incidence of skin cancer and it could have deleterious effects on certain ecosystems. The first concern over O_3 depletion was from NO_x emissions from a fleet of supersonic transport aircraft that would fly through the stratosphere and cause reactions according to equations 3 and 22 (28):

$$NO_2 + O \rightarrow NO + O_2 \tag{22}$$

The net effect of this sequence is the destruction of two molecules of O_3 as one is lost in NO_2 formation and the O of equation 22 would have combined with O_2 to form another. In addition, the NO acts as a catalyst. It is not consumed, and therefore can participate in the reaction sequence many times.

In the mid-1970s, it was realized that the CFCs in widespread use because of their chemical inertness, would diffuse unaltered through the troposphere and into the mid-stratosphere where they, too, would be photolyzed by uv (< 240 nm) radiation. For example, CFC-12 can photolyze:

$$CF_2Cl_2 + uv \rightarrow CF_2Cl + Cl \tag{23}$$

$$CF_2Cl + O_2 \rightarrow CF_2O + ClO \tag{24}$$

forming Cl and ClO radicals that then react with ozone and O:

$$Cl + O_3 \rightarrow ClO + O_2 \tag{25}$$

$$ClO + O \rightarrow Cl + O_2 \tag{26}$$

In this sequence the Cl also acts as a catalyst and two O_3 molecules are destroyed. It is estimated that before the Cl is finally removed from the atmosphere in 1–2 yr by precipitation, each Cl atom will have destroyed ~100,000 O_3 molecules. The estimated O_3-depletion potential of some common CFCs, hydrofluorocarbons, (HFCs), and hydrochlorofluorocarbons, (HCFCs), are presented in Table 4. The O_3-depletion potential is defined as the ratio of the emission

Table 4. **Ozone Depleting Potentials for Industrially Important Compounds**[a]

Compound	Formula	τ (years)[b]	ODP (relative to CFC-11)
methyl bromide	CH_3Br		0.6
tetrachloromethane	CCl_4	47	1.08
1,1,1-trichloroethane	CH_3CCl_3	6.1	0.12
CFC-11	CCl_3F	60	1.0
CFC-12	CCl_2F_2	120	1.0
CFC-13	$CClF_3$		1.0
CFC 113	CCl_2FCClF_2	90	1.07
CFC 114	$CClF_2CClF_2$	200	0.8
CFC 115	CF_3CClF_2	400	0.5
halon 1201	$CHBrF_2$		1.4
halon 1202	CBr_2F_2		1.25
halon 1211	$CBrClF_2$		4.0
halon 1301	$CBrF_3$		16.0
halon 2311	$CHClBrCF_3$		0.14
halon 2401	$CHBrFCF_3$		0.25
halon 2402	$CBrF_2CBrF_2$		7.0
HCFC-22	$CHClF_2$	15	0.055
HCFC-123	$C_2F_3HCl_2$	1.7	0.02
HCFC-124	C_2F_4HCl	6.9	0.022
HCFC-141b	$C_2FH_3Cl_2$	10.8	0.11
HCFC-142b	$C_2F_2H_3Cl$	19.1	0.065
HCFC-225ca	$C_3HF_5Cl_2$		0.025
HCFC-225cb	$C_3HF_5Cl_2$		0.033

[a] Refs. 29, 30.

[b] τ is the tropospheric reaction lifetime (29,30).

rate of a compound required to produce a steady-state O_3 depletion to the amount of CFC-11 required to produce the depletion. The halons, bromochlorofluorocarbons or bromofluorocarbons that are widely used in fire extinguishers, are also ozone-depleting compounds. Although halon emissions, and thus the atmospheric concentrations, are much lower than the most common CFCs, halons are of concern because they are generally more destructive to O_3 than the CFCs.

The strongest evidence that stratospheric O_3 depletion is occurring comes from the discovery of the Antarctic ozone hole. In recent years during the spring, O_3 depletions of 60% or more integrated over all altitudes and 95–100% in some layers have been observed over Antarctica. During winter in the southern hemisphere, a polar vortex develops that prevents the air from outside of the vortex from mixing with air inside the vortex. The depletion begins in August, as the approaching spring sun penetrates into the polar atmosphere, and extends into October. When the hole was first observed, existing chemical models could not account for the rapid O_3 loss, but attention was soon focused on stable reservoir species for chlorine. These compounds, namely, HCl and $ClNO_3$, are formed in competing reactions involving Cl and ClO that temporarily or permanently remove Cl and ClO from participating in the O_3 destruction reactions. For example,

$$Cl + CH_4 \rightarrow HCl + CH_3 \tag{27}$$

$$ClO + NO_2 + M \rightarrow ClNO_3 + M \tag{28}$$

where M is again any third body molecule, remaining unchanged, in the atmosphere.

Heterogeneous reactions, which break down these reservoir species, can occur on the surfaces of cloud particles and play a central role in explaining the magnitude of ozone depletion. Normally the stratosphere is too dry to allow the formation of clouds, however, within the polar vortex, temperatures as low as −90°C allow the formation of polar stratospheric ice clouds. Two main types of clouds have been recognized. Type I clouds contain crystals of nitric acid trihydrate (Type Ia) or sulfuric acid/nitric acid mixtures (Type Ib) and water. Type II clouds are largely frozen water ice. These clouds catalyze the reactions of chlorine reservoir species, such as HCl, and $ClNO_3$. The reservoir species decompose, forming reactive species such as Cl_2 and nitric acid.

$$HCl(s) + ClNO_3 \rightarrow Cl_2 + HNO_3(s) \tag{29}$$

The Cl_2 will photolyze producing atomic chlorine, which participates in gas phase reactions to deplete ozone. The nitric acid remains in the ice, leading to a net removal of nitrogen oxides from the gas phase, which are a sink for ClO (reaction 28). Additional reactions, such as those involving N_2O_5 also occur, and this decomposition of reservoir species dominates the chemistry of ozone depletion.

Regulations designed to mitigate the destruction of stratospheric ozone began in 1976 when the United States banned the use of CFCs as aerosol propellants. No further steps were taken until 1987 when the United States and some 50 other countries adopted the Montreal Protocol. The impact of these

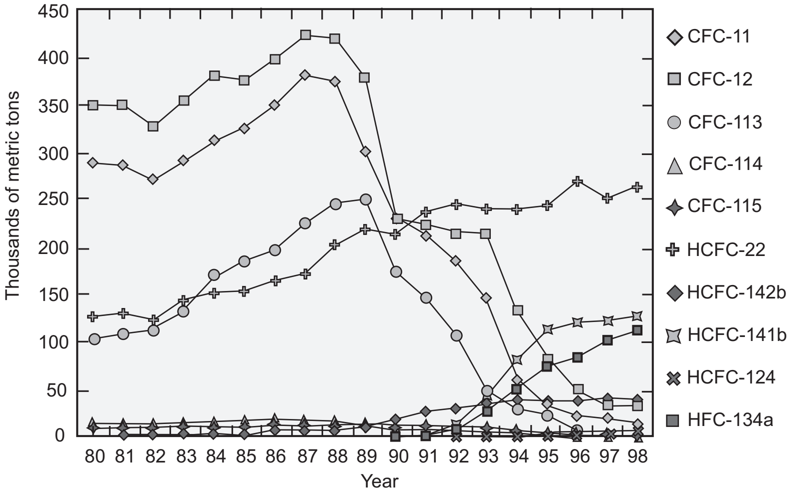


Fig. 11. Annual production rates of ozone depleting compounds 1980–1998 (31).

regulations can be seen in the data presented in Figures 11 and 12. Releases of stratospheric ozone depleting gases reached a peak in the mid-1970s (CFC-11 and CFC 12 combined were ~700 million kg.) Levels have been decreasing since ~1990 (1995 data: 300 million kg., same level as 1966). Yet, atmospheric concentrations are declining relatively slowly, due to the persistence of the ozone depleting gases in the atmosphere.

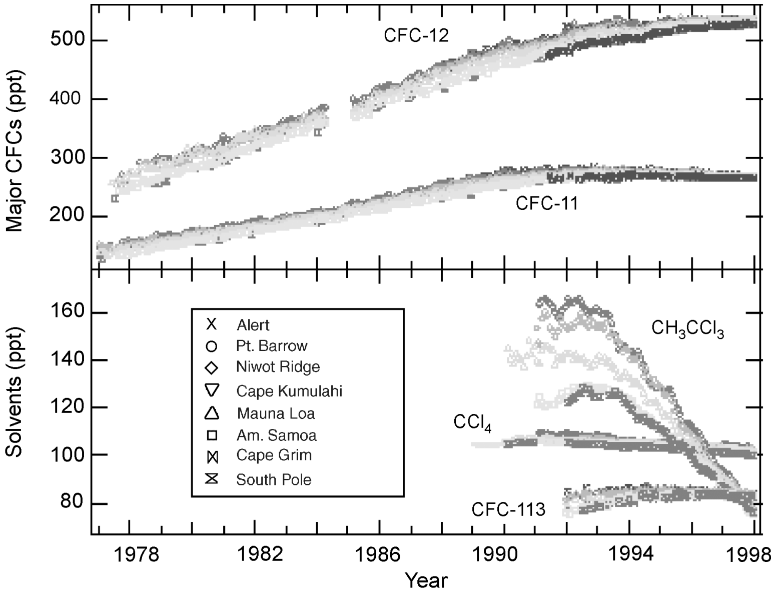


Fig. 12. Recent trends in the tropospheric concentration of CFCs and solvents (32).

4. Air Quality Management

In the United States, the framework for air quality management is the Clean Air Act (CAA), which defines two categories of pollutants: criteria and hazardous. For the hazardous air pollutants, emissions standards are set for selected sources of emissions. Once a substance is designated by EPA as a HAP, EPA has to promulgate a NESHAP (National Emission Standard for Hazardous Air Pollutants), designed to protect public health with an ample margin of safety.

For the criteria pollutants, the CAA charges the EPA with identifying those air pollutants that most affect public health and welfare, and setting maximum allowable ambient air concentrations for these air pollutants. The air pollutants for which national ambient air quality standards are set are referred to as criteria pollutants. Six chemical species (Table 5) have both primary and secondary National Ambient Air Quality Standards (NAAQS). The primary standards are intended to protect the public health with an adequate margin of safety. The secondary standards are meant to protect public welfare, such as damage to crops, vegetation, and ecosystems or reductions in visibility.

The NAAQS apply uniformly across the United States whereas emissions standards for criteria pollutants depend on the severity of the local air pollution problem and whether an affected source already exists or is proposed. In addition, individual states have the right to set their own ambient air quality and emissions standards (which must be at least as stringent as the federal standards) for all pollutants and all sources except motor vehicles. With respect to motor vehicles, the CAA allows the states to choose between two sets of emissions standards: the Federal standards or the more stringent California ones.

To determine if NAAQS are met, states are required to monitor the criteria pollutants' concentrations in areas that are likely to be near or to exceed the standards. If an area exceeds a NAAQS for a given pollutant, it is designated as a nonattainment area for that pollutant, and the state is required to establish an SIP.

The SIP is a strategy designed to achieve emissions reductions sufficient to meet the NAAQS within a deadline that is determined by the severity of the local pollution problem. Areas that receive long (6 years or more) deadlines must show continuous progress by reducing emissions by a specified percentage each year. For SO_2 and NO_2, the initial SIPs were very successful in achieving the NAAQS. For other criteria pollutants, particularly O_3 and to a lesser extent CO, however, many areas have gone through multiple rounds of SIP preparations with little hope of meeting the NAAQS in the near future. If a state misses an attainment deadline, fails to revise an inadequate SIP, or fails to implement SIP requirements, EPA has the authority to enforce sanctions such as banning construction of new stationary sources and withholding federal grants for highways.

In nonattainment areas, the degree of control on small sources is left to the discretion of the state and is largely determined by the degree of required emissions reductions. Large existing sources must be retrofitted with reasonable available control technology (RACT) to minimize emissions. All large new sources and existing sources that undergo major modifications must meet EPAs new source performance standards at a minimum. Additionally, in nonattainment areas, they must be designed using lowest achievable emission rate

Table 5. **Criteria Pollutants and the NAAQS**

	Primary standard (human health related)		Secondary (welfare related)	
Pollutant	type of average	concentration[a]	type of average	concentration
CO [−57%][c] {−22%}[d]	8 h[b]	9 ppm (10 mg/m^3)	no secondary standard	
	1 h[b]	35 ppm (40 mg/m^3)	no secondary standard	
Pb [−94%] {−95%}	maximum quarterly average	1.5 $\mu g/m^3$	same as primary standard	
NO_2 [−25%] {+1%}	annual arithmetic mean	0.053 ppm (100 $\mu g/m^3$)	same as primary standard	
O_3 [−20%]	1 h[e]	0.012 ppm (235 $\mu g/m^3$)	same as primary standard	
	8 h[f]	0.08 ppm (157 $\mu g/m^3$)	same as primary standard	
PM_{10} [−18] {−55%}	annual arithmetic mean	50 $\mu g/m^3$	same as primary standard	
	24-h[g]	150 $\mu g/m^3$	same as primary standard	
$PM_{2.5}$	annual arithmetic mean[h]	15 $\mu g/m^3$	same as primary standard	
	24 h[i]	65 $\mu g/m^3$	same as primary standard	
SO_2 [−50%] {−28%}	annual arithmetic mean	0.03 ppm (80 $\mu g/m^3$)	3 h[b]	0.50 ppm (1300 $\mu g/m^3$)
	24 h[b]	0.14 ppm (365 $\mu g/m^3$)		

[a] Parenthetical value is an equivalent mass concentration.

[b] Not to be exceeded more than once per year.

[c] Air quality concentration, % change 1980–1999.

[d] Emissions, % change 1980–1999.

[e] Not to be exceeded more than once per year on average.

[f] Three-year average of annual fourth highest concentration.

[g] The preexisting form is exceedance based. The revised form is the ninty-ninth percentile.

[h] Spatially averaged over designated monitors.

[i] The form is the ninty-eight percentile.

Source: 40 Code of Federal Register (CFR) Part 50, revised standards issued July 18, 1997. Adapted from U.S. EPA (14)

(LAER) technology, and emissions offsets must be obtained. Offsets require that emissions from existing sources within the area be reduced below legally allowable levels so that the amount of the reduction is greater than or equal to the emissions expected from the new source. RACT usually is less stringent than LAER: It may not be feasible to retrofit certain sources using the LAER technology.

Large sources of SO_2 and NO_x may also require additional emission reductions because of the 1990 Clean Air Act Amendments. To reduce acid deposition, the amendments require that nationwide emissions of SO_2 and NO_x be reduced.

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